

1 **COLD-BOX BINDERS CONTAINING AN EPOXY RESIN, ACRYLATE, AND**
2 **CERTAIN AKYL ESTERS**

3

4 **Field of the Invention**

5 This invention relates to foundry binder systems, which will cure in the presence of sulfur
6 dioxide and a free radical initiator, comprising (a) an epoxy resin; (b) an acrylate; (c) an
7 alkyl ester of a fatty acid, wherein the alkyl group of the ester is an aliphatic hydrocarbon
8 having from 4 to 8 carbon atoms, preferably butyl tallate; and (d) an effective amount of a
9 free radical initiator. The foundry binder systems are used for making foundry mixes. The
10 foundry mixes are used to make foundry shapes (such as cores and molds) which are used
11 to make metal castings, particularly ferrous castings.

12

13 **Description of the Related Art**

14 In the foundry industry, one of the procedures used for making metal parts is “sand
15 casting”. In sand casting, disposable molds and cores are fabricated with a mixture of sand
16 and an organic or inorganic binder. The foundry shapes are arranged in core/mold
17 assembly, which results in a cavity into which molten metal will be poured. After the
18 molten metal is poured into the assembly of molds and cores and cools, the metal part
19 formed by the process is removed from the assembly. The binder is needed so the molds
20 and cores will not disintegrate when they come into contact with the molten metal.

21

22 Two of the prominent fabrication processes used in sand casting are the no-bake and the
23 cold-box processes. In the no-bake process, a liquid curing catalyst is mixed with an
24 aggregate and binder to form a foundry mix before shaping the mixture in a pattern. The
25 foundry mix is shaped by placing it into a pattern and allowing it to cure until it is self-
26 supporting and can be handled. In the cold-box process, a gaseous curing catalyst is passed
27 through a shaped mixture (usually in a corebox) of the aggregate and binder to cure the
28 mixture.

1
2 A cold-box process widely used in the foundry industry for making cores and molds is the
3 "SO₂ cured epoxy/acrylate system". In this process, a mixture of a hydroperoxide (usually
4 cumene hydroperoxide), an epoxy resin, a multifunctional acrylate, typically a coupling
5 agent, and optional diluents, are mixed into an aggregate (sand) and compacted into a
6 specific shape, typically a core or mold. Sulfur dioxide (SO₂), optionally diluted with
7 nitrogen or another inert gas, is blown into the binder/aggregate shape. The shape is
8 instantaneously hardened and can be used immediately in a foundry core/mold system.

9
10 German Patent Application DE 197 27 540 discloses examples of epoxy-acrylic foundry
11 binders containing methyl-, ethyl- and propyl-esters of oleic acid, which are cured with
12 sulfur dioxide in the presence of a free radical initiator.

13
14 **Brief Summary of the Invention**
15 The subject invention relates to foundry binder systems, which cure in the presence of
16 gaseous sulfur dioxide and a free radical initiator, comprising:

17
18 (a) 20 to 70 parts by weight of an epoxy resin;
19 (b) 1 to 50 parts by weight of an acrylate;
20 (c) 1 to 30 parts by weight of an alkyl ester of a fatty acid, wherein the
21 alkyl group of the ester is an aliphatic hydrocarbon having from 4 to
22 8 carbon atoms, preferably butyl tallate; and
23 (d) an effective amount of a hydroperoxide,
24 where (a), (b), (c), and (d) are separate components or mixed with another of said
25 components, provided (b) is not mixed with (d), and where said parts by weight are

1 based upon 100 parts of binder.

2 It has been found that addition of an alkyl ester of a fatty acid to the binder system, wherein
3 the alkyl group of the ester is an aliphatic hydrocarbon having from 4 to 8 carbon atoms,
4 improves the tensile strength development and humidity resistance of cores and molds
5 made with these binders. Preferably used as the epoxy resin is an epoxy resin derived from
6 bisphenol A.

7

8 The foundry binders are used for making foundry mixes. The foundry mixes are used to
9 make foundry shapes, such as cores and molds, which are used to make metal castings.

10

11 **Detailed Description of the Invention**

12 The detailed description and examples will illustrate specific embodiments of the invention
13 will enable one skilled in the art to practice the invention, including the best mode. It is
14 contemplated that many equivalent embodiments of the invention will be operable besides
15 these specifically disclosed. All percentages are percentages by weight unless otherwise
16 specified.

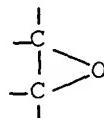
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18 An epoxy resin is a resin having an epoxide group, i.e.,

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30 such that the epoxide functionality of the epoxy resin (epoxide groups per molecule) is
31 equal to or greater than 1.9, typically from 2.0 to 4.0.

1
2 Examples of epoxy resins include (1) diglycidyl ethers of bisphenol A, B, F, G and H, (2)
3 halogen-substituted aliphatic epoxides and diglycidyl ethers of other bisphenol compounds
4 such as bisphenol A,B, F, G, and H, and (3) epoxy novolacs, which are glycidyl ethers of
5 phenolic-aldehyde novolacs, (4) cycloaliphatic epoxy resins, and (5) mixtures thereof.

6
7 Epoxy resins (1) are made by reacting epichlorohydrin with the bisphenol compound in the
8 presence of an alkaline catalyst. By controlling the operating conditions and varying the
9 ratio of epichlorohydrin to bisphenol compound, products of different molecular weight
10 can be made. Epoxy resins of the type described above based on various bisphenols are
11 available from a wide variety of commercial sources.

12
13 Examples of epoxy resins (2) include halogen-substituted aliphatic epoxides, diglycidyl
14 ethers of other bisphenol compounds such as bisphenol A, B, F, G, and H, and epoxy
15 novolac resins. Examples of halogen-substituted aliphatic epoxides include
16 epichlorohydrin, 4-chloro-1, 2-epoxybutane, 5-bromo-1,2-epoxypentane, 6-chloro-1,3-
17 epoxyhexane and the like.

18
19 Examples of epoxy novolacs (3) include epoxy cresol and epoxy phenol novolacs, which
20 are produced by reacting a novolac resin (usually formed by the reaction of orthocresol or
21 phenol and formaldehyde) with epichlorohydrin, 4-chloro-1, 2-epoxybutane, 5-bromo-1,2-
22 epoxypentane, 6-chloro-1, 3-epoxyhexane and the like.

23
24 Examples of cycloaliphatic epoxy resins include any aliphatic, cycloaliphatic, or mixed
25 aliphatic-cycloaliphatic epoxide having any aliphatic groups, and further includes aliphatic
26 epoxy resins having aromatic groups, i.e. mixed aliphatic-aromatic epoxy resins. The
27 aliphatic epoxy resin may contain monomeric epoxide compounds in admixture with

1 polymeric epoxide compounds. The most preferred aliphatic epoxy resins are represented
2 by the following structural formulae:

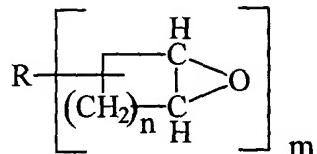
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6 (I)

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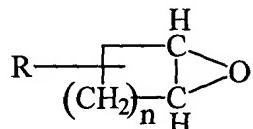


10 where "n" \geq 1 and "m" is a whole number, typically from 1 to 4, preferably from 2-3, or

11

12

13 (II)



16

17 R in structures I and II is predominantly aliphatic in nature, but may contain oxygen
18 functionality as well as mixed aliphatic-aromatic groups. Typically, R is selected from the
19 group consisting of alkyl groups, cycloalkyl groups, mixed alkyl-cycloaliphatic groups, and
20 substituted alkyl groups, cycloalkyl groups, or alkyl-cycloaliphatic groups, where the
21 substituents include, for example, ether, carbonyl, and carboxyl groups.

1
2 Specific examples of aliphatic epoxy resins include 3,4-epoxycyclohexylmethyl-3,4-
3 epoxycyclohexane carboxylate; vinylcyclohexene dioxide; 2-(3,4-epoxycyclohexyl-5,5-
4 spiro-3,4-epoxy) cyclohexane-meta-dioxane; bis-(3,4-epoxycyclohexyl) adipate; 1,2-
5 epoxy-p-vinylcyclohexene; limonene monoxide; limonene dioxide; and hydrogenated
6 bisphenol diglycidyl ethers

7
8 Preferably used are epoxy resins having an average epoxide functionality of at least 2.1 to
9 3.5, preferably from about 2.3 to about 3.0. Particularly preferred are epoxy resins having
10 an average weight per epoxy group of 165 to 200 grams/equivalent.

11
12 The acrylate is a reactive acrylic monomer, polymer, or mixture thereof and contains
13 ethylenically unsaturated bonds. Examples of such materials include a variety of
14 monofunctional, difunctional, trifunctional, tetrafunctional and pentafunctional monomeric
15 acrylates and methacrylates. A representative listing of these monomers includes alkyl
16 acrylates, acrylated epoxy resins, cyanoalkyl acrylates, alkyl methacrylates, cyanoalkyl
17 methacrylates, and difunctional monomeric acrylates. Other acrylates, which can be used,
18 include trimethylolpropane triacrylate, pentaerythritol tetraacrylate, methacrylic acid and 2-
19 ethylhexyl methacrylate. Typical reactive unsaturated acrylic polymers, which may also be
20 used, include epoxy/acrylate reaction products, polyester/urethane/acrylate reaction
21 products, acrylated urethane oligomers, polyether acrylates, polyester acrylates, and
22 acrylated epoxy resins.

23
24
25 Examples of alkyl esters of a fatty acid, wherein the alkyl group of the ester is an aliphatic
26 hydrocarbon having from 4 to 8 carbon atoms, include butyl tallate, isoctyl tallate,
27 isobutylsoyate, and butyl oleate. Preferably used as the alkyl ester of a fatty acid is butyl

1 tallate.

2

3 The free radical initiator is a peroxide and/or hydroperoxide. Examples include ketone
4 peroxides, peroxy ester free radical initiators, alkyl oxides, chlorates, perchlorates, and
5 perbenzoates. Preferably, however, the free radical initiator is a hydroperoxide or a
6 mixture of peroxide and hydroperoxide. Hydroperoxides particularly preferred in the
7 invention include t-butyl hydroperoxide, cumene hydroperoxide, paramenthane
8 hydroperoxide, etc. The organic peroxides may be aromatic or alkyl peroxides.

9

10 Examples of useful diacyl peroxides include benzoyl peroxide, lauroyl peroxide and
11 decanoyl peroxide. Examples of mixed aromatic-aliphatic and aliphatic peroxides
12 respectively include dicumyl peroxide and di-t-butyl peroxide.

13

14 Cumene hydroperoxide and/or a multifunctional acrylate, such as trimethylolpropane
15 triacrylate, may be added to the epoxy resin before mixing it with the foundry aggregate.

16

17 Although solvents are not required for the reactive diluent, they may be used to reduce
18 binder system viscosity or impart other properties to the binder system, such as humidity
19 resistance. Typical solvents used are generally polar solvents, such as liquid dialkyl esters,
20 e.g. dialkyl phthalate of the type disclosed in U.S. Patent 3,905,934, and other dialkyl
21 esters such as dimethyl glutarate, dimethyl succinate, dimethyl adipate, and mixtures
22 thereof. Suitable aromatic solvents are benzene, toluene, xylene, ethylbenzene, alkylated
23 biphenyls and naphthalenes, and mixtures thereof. Preferred aromatic solvents are mixed
24 solvents that have an aromatic content of at least 90% and a boiling point range of 138°C
25 to 232°C. Suitable aliphatic solvents include kerosene. Reactive epoxy resin diluents,
26 such as glycidyl ether, may also be used. If a solvent is used, sufficient solvent should be
27 used so that the resulting viscosity of the epoxy resin component is less than 1,000

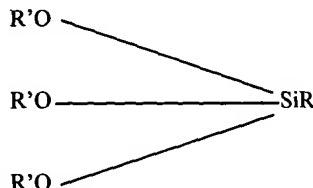
1 centipoise, preferably less than 400 centipoise. Generally, however, the total amount of
2 solvent is used in an amount of 0 to 25 weight percent based upon the total weight of the
3 epoxy resin.

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6 The binder may also contain a silane coupling agent having the following general formula:

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10 wherein R' is a hydrocarbon radical and preferably an alkyl radical of 1 to 6 carbon atoms
11 and R is an alkyl radical, an alkoxy-substituted alkyl radical, or an alkyl-amine-substituted
12 alkyl radical in which the alkyl groups have from 1 to 6 carbon atoms. The silane is
13 preferably added to the Part II binder component in amounts of 0.01 to 2 weight percent,
14 preferably 0.1 to 0.5 weight percent based on the weight of the Part II binder component.

15

16 Polyols may also be used in the foundry binder, e.g. phenolic resins, polyester polyols, and
17 polyether polyols. Of particular interest are phenolic resole resins known as benzylic ether
18 phenolic resole resins, including alkoxy-modified benzylic ether phenolic resole resins and
19 alkoxyLATED versions thereof, which are well known in the art, and are specifically
20 described in U.S. Patent 3,485,797 and 4,546,124.

21

22 It will be apparent to those skilled in the art that other additives such as silicones, release
23 agents, defoamers, wetting agents, etc. can be added to the aggregate, or foundry mix. The
24 particular additives chosen will depend upon the specific purposes of the formulator.

1
2 Typically, the amounts of the components used in the binder system are from 20 to 70 parts
3 by weight of epoxy resin, preferably from 40 to 65 parts by weight; 1 to 50 parts by weight
4 of multifunctional acrylate, preferably from 5 to 30 parts by weight; from 1 to 30 parts of
5 the ester of fatty acid, and preferably from 5 to 25 parts by weight; from 10 to 25 parts by
6 weight of free radical initiator, preferably from 15 to 20 parts by weight, where the parts by
7 weight are based upon 100 parts of the binder system.

8
9 Although the components can be added to the foundry aggregate separately, it is preferable
10 to package the epoxy resin and free radical initiator as a Part I and add to the foundry
11 aggregate first. Then the ethylenically unsaturated material, as the Part II, either alone or
12 along with some of the epoxy resin, is added to the foundry aggregate.

13
14 Various types of aggregate and amounts of binder are used to prepare foundry mixes by
15 methods well known in the art. Ordinary shapes, shapes for precision casting, and
16 refractory shapes can be prepared by using the binder systems and proper aggregate. The
17 amount of binder and the type of aggregate used are known to those skilled in the art. The
18 preferred aggregate employed for preparing foundry mixes is sand wherein at least about
19 70 weight percent, and preferably at least about 85 weight percent, of the sand is silica.
20 Other suitable aggregate materials for ordinary foundry shapes include zircon, olivine,
21 aluminosilicate, chromite sands, and the like.

22
23 In ordinary sand type foundry applications, the amount of binder is generally no greater
24 than about 10% by weight and frequently within the range of about 0.5% to about 7% by
25 weight based upon the weight of the aggregate. Most often, the binder content for ordinary
26 sand foundry shapes ranges from about 0.6% to about 5% by weight based upon the weight
27 of the aggregate in ordinary sand-type foundry shapes.

1
2 The foundry mix is molded into the desired shape by ramming, blowing, or other known
3 foundry core and mold making methods. The shape is then cured almost instantaneously
4 by the cold-box process, using vaporized sulfur dioxide as the curing agent (most typically
5 a blend of nitrogen, as a carrier, and sulfur dioxide containing from 35 weight percent to 65
6 weight percent sulfur dioxide), described in U.S. Patent 4,526,219 and 4,518,723, which
7 are hereby incorporated by reference. The shaped article is preferably exposed to effective
8 catalytic amounts of gaseous sulfur dioxide, and, optionally, minor amounts of a carrier gas
9 can be used. The exposure time of the sand mix to the gas is typically from 0.5 to 10
10 seconds. The foundry shape is cured after gassing with sulfur dioxide. Oven drying is
11 needed if the foundry shape is coated with a refractory coating.

12
13 The core and/or mold may be formed into an assembly. When making castings, the
14 assembly may be coated with a water-based refractory coating and passed through a
15 conventional or microwave oven to remove the water from the coating.

ABBREVIATIONS

¹⁸ The abbreviations used in the examples are as follows:

20 Bis-A epoxy bisphenol-A epoxy resin, having a functionality of 1.9, an
21 epoxide equivalent weight of about 184-192 g/eq, and a
22 viscosity of about 13,000 cp.

24 BT butyl ester of tall oil fatty acid, PLASTHALL 503 from CP
25 Hall.

27 CHP cumene hydroperoxide.

- 1
- 2 ISOSET® 4304 (Part I) acrylate-free epoxy resin component containing bis A epoxy
- 3 resin and CHP in a weight ratio of about 65to 35
- 4
- 5 ISOSET® 4305 NS (Part II) epoxy resin component containing bis A epoxy resin,
- 6 TMPTA and a silane coupling agent, such that the amount of
- 7 epoxy resin is about 55 weight percent and the amount of
- 8 TMPTA is about 45 weight percent.
- 9
- 10 ISOSET® 4315 (Part II) epoxy resin component containing bis A epoxy resin,
- 11 TMPTA, a dibasic ester solvent, an aliphatic solvent, and a
- 12 silane coupling agent, such that the amount of epoxy resin is
- 13 about 40 weight percent and the amount of TMPTA is about
- 14 25 weight percent.
- 15
- 16
- 17 ISOSET® 4525 (Part II) epoxy resin component containing bis A epoxy resin,
- 18 TMPTA, a dibasic ester solvent, and an aliphatic solvent,
- 19 such that the amount of epoxy resin is about 50 weight
- 20 percent and the amount of TMPTA is about 40 weight
- 21 percent.
- 22
- 23 MS methyl ester of soybean oil, ME-130 sold by Lambert
- 24 Technologies.
- 25
- 26 OT isoocetylallate, PLASTHALL 100 sold by CP Hall.

RME rapeseed methyl ester, Connester 6020 sold by OELMUEHLE LEER of Germany.

EXAMPLES

7 While the invention has been described with reference to a preferred embodiment, those
8 skilled in the art will understand that various changes may be made and equivalents may be
9 substituted for elements thereof without departing from the scope of the invention. In
10 addition, many modifications may be made to adapt a particular situation or material to the
11 teachings of the invention without departing from the essential scope thereof. Therefore, it
12 is intended that the invention not be limited to the particular embodiment disclosed as the
13 best mode contemplated for carrying out this invention, but that the invention will include
14 all embodiments falling within the scope of the appended claims. In this application, all
15 units are in the metric system and all amounts and percentages are by weight, unless
16 otherwise expressly indicated.

Testing Protocol

19 The binder formulations were evaluated in the following examples for their tensile
20 strengths. ISOSET®4304/4525 binder, which did not contain an ester of a fatty acid, was
21 used as the control. BT and OT were added to the Part I to see what effect the addition had
22 on the binder and cores made from the binder. Comparison examples were carried out
23 using methyl esters of fatty acids, e.g. RME or MS instead of BT and OT. In the
24 formulations containing the ester of the fatty acid in the Part I, 25 percent by weight of the
25 fatty acid ester was used based upon the total weight of the Part I, unless otherwise
26 indicated.

1 The components were mixed for 4 minutes using a Hobart sand mixer. The binders were
2 prepared and all cores were made on a Gaylord MTB-3 core-blowing unit. SO₂ cured
3 tensile test specimens were gassed 0.50 seconds with a 65/35 SO₂/nitrogen mixture
4 delivered by an MT Systems SO₂/Nitrogen blending unit followed by a 10 second dry air
5 purge. The binder level was 1.0% based on the weight of the sand.

6

7 **Measurement of Tensile Strength**

8 How well a binder system bonds an aggregate (sand) together is typically evaluated by
9 comparing tensile strength measurements of test cores made with the binder. Sufficient
10 core strength is needed once the binder/sand mix is cured to prevent the core from
11 distorting or cracking during assembly operations. Tensile strength measurements are
12 taken immediately (20 seconds after core box opens), 5-minutes, one-hour, 24-hours and
13 24 hours at 90% relative humidity. Binder systems that retain higher tensile strengths over
14 time can better retain their dimensional accuracy and have less core breakage problems.
15 All tensile strength measurements were measured in accordance with standard ASTM tests.

16

17 A description of the formulations used and the resulting tensile strengths of test cores made
18 with the binder are set forth in Tables I, II, and III.

1

**Table I: Control A
Examples 1 & 2
Comparative Examples B & C**

	Control A	Examples		Comp. Examples	
		1	2	B	C
Part I	ISOSET 4304	+25% BT	+ 25% OT	+ 25% RME	+25% MS
Part II	ISOSET 4305 NS	4305NS	4305 NS	4305 NS	4305 NS
Part I/II	60/40	60/40	60/40	60/40	60/40
Tensile Strength [psi]					
Imm	77	86	104	72	63
5 Min	138	156	172	124	122
1 h	179	198	198	159	154
24 h	185	241	232	198	181
24 h/90% rh	136	183	184	145	128

2

3

**Table II: Control D
Examples 3 & 4
Comparative Examples E & F**

	Control D	Examples		Comp. Examples	
		3	4	E	F
Part I	ISOSET 4304	+25% BT	+ 25% OT	+ 25% RME	+25% MS
Part II	ISOSET 4315	4315	4315	4315	4315
Part I/II	60/40	60/40	60/40	60/40	60/40
Tensile Strength [psi]					
Imm	60	71	77	48	59
5 Min	104	134	140	85	122
1 h	140	180	175	111	153
24 h	191	228	219	144	187
24 h/90% rh	142	182	174	144	148

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**Table III: Control G
Examples 5 & 6
Comparative Examples H & I**

	Control G	Examples		Comp. Examples	
		5	6	H	I
Part I	ISOSET 4304	+25% BT	+ 25% OT	+ 25% RME	+25% MS
Part II	ISOSET 4525	4525	4525	4525	4525
Part I/II	60/40	60/40	60/40	60/40	60/40
Tensile Strength [psi]					
Imm		70	78	90	63
5 Min		128	141	151	116
1 h		158	173	183	148
24 h		179	220	225	190
24 h/90% rh		129	176	174	140
					126

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The data in Tables I-III indicate that the formulations with BT and OT provide higher over all tensile strengths than the control and similar formulations using RME and MS.